

PROFORMA OF EVENT

1. Name of Department:- CHEMISTRY
2. Event:- SEMINAR
3. Venue: Hall- 12
4. Date:-15.12.2016 & Time-2.30pm
5. Title of the Topic:- Application of Crystal Field Theory to Tetrahedral and Octahedral Coordinated Compounds
6. Name and Designation of the Resource Person:- Sri Prafulla Kumar Behera

Asst. Professor S.S.B, Mahavidyalaya, Mahakalapada

Brief Introduction of the Resource Person:- Sri Prafulla Kumar Behera has qualified NET during 2015 and GATE during 2016. His area of Specialization is Organic Chemistry

Name of Presiding person:- Dr. Heeramani Behura

Principal, TWC, Kendrapara

Convener :- Mrs. Pramilarani Behera, HoD, Chemistry

ABSTRACT

Octahedral crystal field stabilization energy. Degenerate atomic *d*-orbitals of a free metal ion (left), The Crystal Field Theory (CFT) is a model for the bonding interaction between transition metals and ligands. ... Therefore, the *d* electrons closer to the ligands will have a higher energy than those further away, which results in the *d* orbitals splitting in energy. This splitting is affected by: the nature of the metal ion. Crystal Field Splitting in Octahedral Complex. This splitting of degenerate level in the presence of ligand is known as crystal field splitting. The difference between the energy of t_{2g} and e_g level is denoted by " Δ_o " (subscript o stands for octahedral). The following points will clearly state the limitations of crystal field theory:

1. The assumption that the interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.
2. This theory takes only *d*-orbitals of a central atom into account. The *s* and *p* orbitals are not considered for the study.
3. The theory fails to explain the behaviour of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H_2O is a stronger ligand as compared to OH^- .
4. The theory rules out the possibility of having *p* bonding. This is a serious drawback because it is found in many complexes.
5. The theory gives no significance to the orbitals of the ligands. Therefore, it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals.

According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five degenerate d-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the *d*-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the *d*-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the *d*-electrons closer to the ligands will have a higher energy than those further away which results in the *d*-orbitals splitting in energy. This splitting is affected by the following factors:

- the nature of the metal ion.
- the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
- the arrangement of the ligands around the metal ion.
- the coordination number of the metal (i.e. tetrahedral, octahedral...)
- the nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy *d* groups.

The most common type of complex is octahedral, in which six ligands form the vertices of an octahedron around the metal ion. In octahedral symmetry the *d*-orbitals split into two sets with an energy difference, Δ_{oct} (the crystal-field splitting parameter, also commonly denoted by $10Dq$ for ten times the "differential of quanta") where the d_{xy} , d_{xz} and d_{yz} orbitals will be lower in energy than the d_z^2 and $d_{x^2-y^2}$, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experiences less repulsion. The three lower-energy orbitals are collectively referred to as t_{2g} , and the two higher-energy orbitals as e_g . Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting, the *d*-orbitals again split into two groups, with an energy difference of Δ_{tet} . The lower energy orbitals will be d_z^2 and $d_{x^2-y^2}$, and the higher energy orbitals will be d_{xy} , d_{xz} and d_{yz} - opposite to the octahedral case. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the *d*-orbitals, the energy splitting will be lower than in the octahedral case. Square planar and other complex geometries can also be described by CFT. The size of the gap Δ between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of Δ , while others always give a large splitting. The reasons behind this can be explained by ligand field theory. The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ , $I^- < Br^- < S^{2-} < SCN^-$ (S-bonded) $< Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$ (N-bonded) $< CH_3CN < py < NH_3 < en < 2,2'$ -bipyridine $< phen < NO_2^- < PPh_3 < CN^- < CO$. The oxidation state of the metal also contributes to the size of Δ between the high and low energy levels. As the oxidation state increases for a given metal, the magnitude of Δ increases. A V^{3+} complex will have a larger Δ than a V^{2+} complex for a given set of ligands, as the difference in charge density allows the ligands to be closer to a V^{3+} ion than to a V^{2+} ion. The smaller distance between the ligand and the metal ion results in a larger Δ , because the ligand and metal electrons are closer together and therefore repel more. The use of these splitting diagrams can aid in the prediction of magnetic properties of coordination compounds. A compound that has unpaired electrons in its splitting diagram will be paramagnetic and will be attracted by magnetic fields, while a compound that lacks unpaired electrons in its splitting diagram will be diamagnetic and will be weakly repelled by a magnetic field.

The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the *d*-orbitals are split in a ligand field (as described above), some of them become lower in energy than

before with respect to a spherical field known as the barycenter in which all five d -orbitals are degenerate. For example, in an octahedral case, the t_{2g} set becomes lower in energy than the orbitals in the barycenter. As a result of this, if there are any electrons occupying these orbitals, the electrons in the lower orbitals is canceled out by the destabilizing effect of the electrons in the upper orbitals.

the metal ion is more stable in the ligand field relative to the barycenter by an amount known as the CFSE. Conversely, the e_g orbitals (in the octahedral case) are higher in energy than in the barycenter, so putting electrons in these reduces the amount of CFSE. Destabilization of d -orbitals within a spherical negative electric field (center), and loss of degeneracy relative to the spherical field when ligands are treated as point charges in an octahedral geometry.

If the splitting of the d -orbitals in an octahedral field is Δ_{oct} , the three t_{2g} orbitals are stabilized relative to the barycenter by $\frac{2}{5} \Delta_{\text{oct}}$, and the e_g orbitals are destabilized by $\frac{3}{5} \Delta_{\text{oct}}$. As examples, consider the two d^5 configurations shown further up the page. The low-spin (top) example has five electrons in the t_{2g} orbitals, so the total CFSE is $5 \times \frac{2}{5} \Delta_{\text{oct}} = 2\Delta_{\text{oct}}$. In the high-spin (lower) example, the CFSE is $(3 \times \frac{2}{5} \Delta_{\text{oct}}) - (2 \times \frac{3}{5} \Delta_{\text{oct}}) = 0$ - in this case, the stabilization generated by the electrons in the lower orbitals is canceled out by the destabilizing effect of the electrons in the upper orbitals.

REPORT: One day Seminar was organized by the department of Chemistry in Hall no.12 on dated 15.12.2016 at 2.30pm. Welcome address was delivered by Mrs. Pramilarani Behera, HoD Chemistry. Mr. Prafulla kumar Behera, Asst. Professor in Chemistry, SSB, Mahavidyalaya as the resource person, delivered about the Application of Crystal Field Theory to Tetrahedral and Octahedral Coordinated Compounds. Around 61 participants were present and interacted with the resource person. The Seminar was ended with vote of thanks by Mrs. Lipika Rout, Demonstrator in Chemistry.

Photos of the Event:-







